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Published in:
Journal of Chemical Physics

DOI:
10.1063/1.2872941

Published: 01/01/2008

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

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Citation: J. Chem. Phys. 128, 154707 (2008); doi: 10.1063/1.2872941
View online: http://dx.doi.org/10.1063/1.2872941
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v128/i15
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Molecular dynamics simulation of phase separating binary liquids in cylindrical Couette flow

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(Received 31 October 2007; accepted 24 January 2008; published online 16 April 2008)

We use molecular dynamics simulations to study phase separation of a 50:50 (by volume) fluid mixture in a confined and curved (Taylor–Couette) geometry, consisting of two concentric cylinders. The inner cylinder may be rotated to achieve a shear flow. In nonsheared systems we observe that, for all cases under consideration, the final equilibrium state has a stacked structure. Depending on the lowest free energy in the geometry the stack may be either flat, with its normal in the z direction, or curved, with its normal in the r or θ direction. In sheared systems we make several observations. First, when starting from a prearranged stacked structure, we find that sheared gradient and vorticity stacks retain their character for the durations of the simulation, even when another configuration is preferred (as found when starting from a randomly mixed configuration). This slow transition to another configuration is attributed to a large free energy barrier between the two states. In case of stacks with a normal in the gradient direction, we find interesting interfacial waves moving with a prescribed angular velocity in the flow direction. Because such a wave is not observed in simulations with a flat geometry at similar shear rates, the curvature of the wall is an essential ingredient of this phenomenon. Second, when starting from a randomly mixed configuration, stacks are also observed, with an orientation that depends on the applied shear rate. Such transitions to other orientations are similar to observations in microphase separated diblock copolymer melts. At higher shear rates complex patterns emerge, accompanied by deviations from a homogeneous flow profile. The transition from steady stacks to complex patterns takes place around a shear rate 1/τ_dv, where τ_dv is the crossover time from diffusive to viscous dominated growth of phase-separated domains, as measured in equilibrium simulations.

I. INTRODUCTION

The kinetics of phase separation in binary liquids has been of a great interest over the years. It is usually described by the time dependence of some characteristic length R in the system, representing the size of the phase separated domains. It has proven difficult to construct a theory describing the time evolution of these length scales, mainly because the dynamics of phase separation is nonlinear and involves moving interfaces. Scaling analysis of the Navier–Stokes and Cahn–Hilliard equations present a reasonable picture for different exponents involved in the process in the viscous regime.\(^1\) Based on self-similar growth of patterns these predict that the characteristic length scale grows as a power law in time, i.e., \(R(t) \propto t^\alpha\). The exponent reported for a non-sheared system is \(\alpha=2/3\) and \(\alpha=1\) for two- and three-dimensional binary fluid mixtures, respectively.

Shear flow causes an additional pattern formation in phase separating mixtures which is very interesting and not completely understood. Pattern formation plays a central role in the formation of various structures in complex fluids such as polymers, colloids, liquid crystals, and self-assembling membranes and micelles. The (shear) rheology of phase separating complex liquids is thus very important from both a physical and an engineering point of view.

Theoretically, the case of phase separating liquids under shear is very complex due to the coupling of bulk flow with the hydrodynamic modes of the interface. Shear flow is found to introduce anisotropy in the growth law of the domains. The exponent \(\alpha\) obtained by renormalization group theory is greater than 1 in the velocity (parallel) direction and close to 1/3 in gradient (perpendicular) direction.\(^2\) This suggests that shear enhances the growth in the velocity direction but suppresses it in the gradient direction. This seems to be confirmed by experiments.\(^3\) Different time scales are involved in the breakup and coalescence of a domain. Depending on the ratio between these time scales and the deformation time scale of the flow, different metastable states are observed. For this no theory is available.

Simulations may help in gaining insight in the dynamics of phase separating systems. Phase separating binary liquids have mostly been studied by lattice Boltzmann\(^9\)–\(^12\) (LB) and by molecular dynamics\(^13\)–\(^14\) (MD) simulations. Many of the early simulations were limited to two-dimensional non-sheared systems, but recent advances in computational power have moved the scope to three-dimensional systems as well. The observed domain growth scaling laws are gen-

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In general agreement with the theoretical predictions. During the last decade also simulations of phase separating systems undergoing shear have been carried out, both by LB (Refs. 11–14) and MD.15,16 In these studies it was observed that the interplay between surface tension and deformation due to shear gives rise to various growth patterns like stretched domains and string phases in the direction of shear. Very recently it has been shown that a nonequilibrium (dynamical) steady state is reached, in which the domains attain a finite length instead of growing indefinitely.12–14 The finite length is a result of interference of the shear flow with the transition from an interfacial/viscous to an interfacial/inertial regime and is found to decrease with increasing shear rate. The Reynolds number, defined as \( Re = \frac{\gamma R^2}{\nu} \), where \( \gamma \) is the shear rate, \( R \) is the domain size and \( \nu \) is the kinematic viscosity, varied between 260 and 2300 in the three-dimensional LB simulations.13 Perhaps counterintuitively the lowest \( Re \) corresponded to the highest shear rate.

In this work we will show the influence of a different mechanism, namely one where (thermal) diffusive growth of domains is counterbalanced by convection with the flow. Suppression of domain growth at high shear rates by this mechanism is relevant to phase separating colloidal systems in, e.g., microdevices. This diffusion-convection mechanism is not active in the quoted LB simulations because thermal diffusion is not included in the model. Another difference is that the LB simulations have focused on the bulk behavior of phase separating systems under planar shear. In this paper we take the opposite stand and focus on the influence of confining walls and the curvature of these walls. We think this is interesting because even without shear, walls can structure and orient the phase separating domains. The precise orientation of the fully phase separated domains will depend on the relative values of fluid-fluid and fluid-wall surface tensions. What happens when such systems are sheared is an open question we wish to address.

In this work we study phase separation of a 50:50 (by volume) fluid mixture in a three-dimensional Taylor–Couette geometry (two concentric cylinders), both with and without shear flow. We restrict ourselves to reporting interesting observations. We will show that for low and moderate shear rates the final phase separated systems have a banded structure with stacks oriented in a direction that depends on the inner and outer radius of the Couette cell and the applied shear rate. We will also show that at high shear rates complex patterns emerge because the (thermal) diffusive growth of domains is counterbalanced by convection with the flow. This is accompanied by deviations from a homogeneous flow profile. The paper is organized as follows. In Sec. II we present the simulation details. In Sec. III we discuss the results obtained from different configurations and shear rates. In the final section we present the conclusions.

II. SIMULATION SETUP

In our simulations, the interactions between like particles are based on the Lennard-Jones potential

\[
U_{LJ}(r_{ij}) = 4\epsilon \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6},
\]

(1)

where \( \epsilon \) and \( \sigma \) are the strength and range, respectively, and \( r_{ij} \) is the distance between particles \( i \) and \( j \). Both the potential and the derived force are smoothly truncated at the cutoff distance \( r_c = 2.5 \sigma \), to eliminate discontinuities at the latter distance. Unlike particles interact by the purely repulsive WCA (Weeks-Chandler-Andersen) potential, defined by

\[
U_{WCA}(r) = \begin{cases} 
4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} & (r \leq 2^{1/6}\sigma) \\
0 & (r > 2^{1/6}\sigma)
\end{cases}
\]

(2)

In our simulations, Newton’s equations of motion are integrated numerically using the Verlet leap-frog algorithm with a time step \( \Delta t = 0.002\tau \) for low shear rate runs and \( \Delta t = 0.0005\tau \) for higher shear rates, where \( \tau = \sqrt{m\sigma^2/\epsilon} \) and \( m \) is the mass of a particle. The temperature used in the simulations is \( k_B\theta = 1.0\epsilon \), where \( k_B \) is the Boltzmann’s constant. To dissipate the energy released by the phase separating system and shear, we use a thermostat. Many thermostats interfere with the creation of hydrodynamic flow fields and therefore are not suited for the study of the later stages of phase separation. We have used the friction and random forces of dissipative particle dynamics24,25 (DPD) to thermostat the system, both because of its conservation of local momentum, which is also the basis of the Navier–Stokes equation, and because of its avoidance of a profile bias in boundary driven nonequilibrium simulations of shear flow.26 In DPD the friction force \( \mathbf{F}_{\text{fric}} \) and random force \( \mathbf{F}_{\text{ran}} \) between a pair of particles separated by a distance \( r \) within the cutoff distance \( r_c \) is given by

\[
\mathbf{F}_{\text{fric}} = -\frac{\kappa}{2\sqrt{\Delta t}} \left( 1 - \frac{r}{r_c} \right)^2 \left( \mathbf{\hat{r}} \cdot \Delta \mathbf{v} \right) \mathbf{\hat{r}},
\]

(3)

\[
\mathbf{F}_{\text{ran}} = \frac{\kappa}{\sqrt{\Delta t}} \left( 1 - \frac{r}{r_c} \right) \zeta \mathbf{\hat{r}},
\]

(4)

where \( \kappa \) is the strength of the friction constant, which we set equal to \( 3\epsilon r^{1/2}\sigma^{-1} \). In this work, \( \mathbf{\hat{r}} \) is the unit vector in the direction of the line joining the two particles, \( \Delta \mathbf{v} \) is the velocity difference between the particle pair, and \( \zeta \) is a random number with zero mean and unit variance.

To see the effect of confinement and curvature, we simulate a Taylor–Couette geometry with different radii for the inner and outer (concentric) cylinders. In particular, in one of three sets we fix the inner radius to \( R_1 = 40\sigma \) and vary the outer radius between \( R_2 = 55\sigma \) and \( 80\sigma \), so that the inner to outer radius ratio is \( R_1/R_2 = 0.5–0.73 \). In the second set we use an inner radius of \( R_1 = 25\sigma \) and an outer radius of \( R_2 = 65, 70\sigma \). For the third set we use \( R_1 = 15\sigma \) and \( R_2 = 60, 65\sigma \). In all these simulations is fixed at \( \rho = 0.7\sigma^{-3} \). When changing the outer radius \( R_2 \), the height \( Z \) of the box is changed accordingly in order to keep the total volume constant.

To keep the system size manageable we simulate a periodic system with an overall angle of \( \Theta_0 = \pi/3 \), as schematically shown in Fig. 1. The total number of particles is 30 000 for simulations starting from a banded state, and 60 000 for
simulations starting from randomly mixed configurations. We apply shear by rotating the inner wall with an angular velocity \( \omega \) ranging from 0.001 to 0.1 \( r^{-1} \).

Since we simulate only part of a Couette cell, the periodic boundary conditions need to be modified accordingly. Periodic boundary conditions in the \( z \) direction are applied as usual. In order to impose periodic boundary conditions in the \( \theta \) direction, both for calculating forces between particles on either side of the boundaries and for replacing a particle from one boundary to the other, it is necessary to rotate force and velocity vectors. Specifically, to calculate the velocity \( \mathbf{v}' \) of an image particle in the periodic box directly following the central box in the positive \( \theta \) direction, it must be calculated from the velocity \( \mathbf{v} \) of the original particle in the central box by a rotation

\[
\begin{pmatrix}
  u'_r \\
  u'_\theta \\
  u'_z
\end{pmatrix} =
\begin{pmatrix}
  \cos(\Theta_r) & -\sin(\Theta_r) & 0 \\
  \sin(\Theta_r) & \cos(\Theta_r) & 0 \\
  0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
  u_r \\
  u_\theta \\
  u_z
\end{pmatrix}.
\]

A similar rotation applies, with \( \Theta_r \) substituted by \(-\Theta_r\), in case of an image particle in the periodic box preceding the central box in the \( \theta \) direction.

In the \( r \) direction a wall is present at \( R_1 \) and \( R_2 \). A bounce back rule (inversion of the velocity \( \mathbf{v} \rightarrow -\mathbf{v} \)) is applied to any particle colliding with the wall. For moving walls, this bounce back rule is relative to a frame comoving with the wall. Despite the bounce back rule, without additional measures, we found a small amount of slip at the walls, especially at the higher shear rates. To make sure that the shear is applied properly and there is no slip at the wall, all particles within one \( \sigma \) distance from the walls are given a new velocity from a Maxwell–Boltzmann distribution, whose average is shifted in the \( \theta \) direction to match the velocity of the wall. In this way walls provide stick boundary conditions and at the same time act as a thermostat.

III. RESULTS AND DISCUSSION

We perform three different types of (computer) experiments in our Couette geometry. (i) In the first series of experiments we start with randomly mixed configurations and study phase separation without shear. (ii) In the second we start from fully phase separated systems, under various geometrical conditions, and then suddenly start shear. (iii) In the third series of experiments we start from randomly mixed configurations and then analyze the effect of the onset of shear.

A. No shear

In the first series of experiments we do not apply shear. In this case simple free energy calculations, as given in Appendix A, suffice to predict the final equilibrium states. For example, when fixing the inner radius, varying the outer radius at constant volume changes the relative free energy between different final equilibrium states. In Fig. 2 we have plotted free energies for various configurations defined later. We have simulated geometries with inner radius \( R_1 = 40 \sigma \) and outer radius from the set of \( R_2 = 55, 60, 65, 75, 80 \sigma \). The outer radii were carefully chosen to ensure different final configurations.

For the narrowest configuration, with outer radius \( R_2 = 55 \sigma \), the equilibrium configuration predicted by free energy calculations consists of two separated phases, stacked along the \( z \) direction (here and in the following we call these \( z \) stacks). This is also observed in our simulations, see Fig. 3. For a slightly less narrow configuration, when the outer radius is \( R_2 = 60 \sigma \), the predicted equilibrium configuration consists of stacks with their normal in the \( \theta \) direction (\( \theta \) stacks), which is verified in our simulations as well.

The next geometry, \( R_2 = 65 \sigma \), shows an interesting pattern. According to the free energy calculations the \( \theta \) stack still has the lowest free energy, but in our simulation a cy-

![FIG. 1. Simulated Taylor–Couette cell geometry. Stick boundary walls are present at \( r=R_1 \) and \( r=R_2 \). In the sheared simulations the inner wall is rotating. Periodic boundaries are applied in the flow direction at \( \theta=0 \) and \( \theta=\Theta_r \), and in the vorticity direction at \( z=0 \) and \( z=Z \).](image-url)

![FIG. 2. Interfacial area between the A and B phases for the case \( R_1 = 40 \sigma \) and a fixed volume of 42.857\( \sigma^3 \) (30 000 particles). The arrows indicate the values of \( R_2 \) studied here. We consider the cases of \( r \), \( \theta \), and \( z \) stacks, as well as a cylindrical drop at the outer wall. For equally wetting liquids, the configuration of lowest interfacial area is the configuration of lowest free energy.](image-url)

![FIG. 3. (Color) Phase separated configurations for \( R_1 = 40 \sigma \) and various \( R_2 \) at a fixed volume of 42.857\( \sigma^3 \) (30 000 particles). For \( R_2 = 55 \sigma \) we look from the axis of the cylinder toward the inner wall in the \( z-\theta \) plane. For all other values of \( R_2 \) we show the top view (\( r-\theta \) plane).](image-url)
lindrical drop forms at the outer radius, see Fig. 3. During the course of our simulation it remains like this. Free energy calculations which also consider the cylindrical drop suggest that this is a metastable state with a free energy very close to that of the \( \theta \) stacks. The system is able to stay in this configuration for a prolonged time. We expect that \( \theta \) stacks will eventually form, but our equilibrium simulations are not long enough to observe this transition.

The next two systems also show interesting behavior. Theoretically, \( R_2=75\sigma \) corresponds to a final equilibrium state of two concentric liquid cylinders (\( r \) stacks in our language). It appears to be very difficult for the liquid in absence of shear to have a stable curved interface and the phase separation observed is a stack in the \( \theta \) direction, which is the next lowest free energy configuration. For the last system (\( R_2=80\sigma \)), it is clear from Fig. 2 that again \( r \) stacks (concentric liquid cylinders) should form the most stable configuration, but in the simulation the system is trapped in a metastable state of multiple cylindrical droplets on either wall. These drops keep moving but within the course of our simulation they do not merge to a final state.

In summary, for the narrow systems we observe full phase separation in agreement with free energy calculations, while for the wider systems we observe configurations that are stuck in metastable states, which are often the next lowest free energy configurations.

B. With shear, starting from phase separated systems

Before studying the influence of shear on the kinetics of phase separation we investigate what shear does with the equilibrium configurations going with particular geometries. We focus on three different geometries with \( R_1=40\sigma \) and \( R_2=55, 65, 75\sigma \). As we have seen earlier, without shear the first corresponds to a final equilibrium of \( z \) stacks, the second to \( \theta \) stacks, and the third to \( r \) stacks. For each of these geometries we start with three different initial conditions, namely stacks in the \( r \), \( \theta \), or \( z \) direction. Obviously, only one of them corresponds to the equilibrium situation without shear. We apply two different shear rates by rotating the inner wall with an angular velocity of \( \omega=0.01 \) or \( 0.1 \) rad \( \tau^{-1} \).

One feature which is common to both \( z \) (vorticity) and \( r \) (gradient) stacks is the extreme slowness of transitions from one configuration to another. Starting from a stack in the \( z \) direction, the system continues to be \( z \) stacked for the duration of the simulation, at both shear rates studied. This includes geometries which would not prefer to form \( z \) stacks at rest, nor if we would start from a randomly mixed simulation. Analogous results are obtained starting from stacks in the \( r \) direction. Although we are not able yet to quantify the effect, it can qualitatively be explained on the basis of existing free energy barriers. Thermal fluctuations and shear are not enough to overcome the free energy barrier in the time simulated.

It is impossible for \( \theta \) stacks to persist when the inner wall is rotating, so such configurations must quickly disappear and change to other configurations. Figure 4 shows that if we start from a stack in the \( \theta \) (flow) direction, streaks are quickly elongated along the flow direction, which are then pushed in the outward direction. These moving bands merge and then result in stacks in the \( z \) direction. These \( z \) stacks are stable for all shear rates applied in our simulations. Notice that the view toward the axis will be one of bands stacked along the vorticity direction.

In case of \( r \) stacks an interesting phenomenon occurs in Couette shear flow: a single interfacial crest develops at the interface which moves like a soliton in the flow direction (we use the word solitonlike, because we do not imply the rather specific meaning of a soliton in the context of nonlinear, dispersive waves, but rather its characteristics of a localized “heap” that is moving in space without changing shape). At low shear rates this interfacial heap is barely visible but at higher shear rates it is very prominent, as shown in Fig. 5. The curvature of the wall is an essential ingredient of this phenomenon because no heap is observed in simulations containing the same phase-separated fluid in a planar shear geometry with the same gap width and subjected to the same shear rates. We will now analyze the angular velocity of the heap. Let the radial coordinate of the interface for each value of \( \theta \) and \( r \) be given by \( R(\theta, t) \). The solitonlike character may then be expressed as

\[
R(\theta, t) = R(\theta - \Omega t, 0),
\]

where \( \Omega \) is the angular velocity of the heap. To measure this velocity we must be careful not to measure the velocities of the individual particles, but only their collective effect on the interfacial perturbation. To this end we define

FIG. 4. (Color) Evolution of a sheared system containing preassembled \( \theta \) stacks. In this particular case \( R_1=40, R_2=65\sigma \), and \( \omega=0.1\tau^{-1} \). The first two figures are top views \((r-\theta \text{ plane})\), in the last figure we look from the inside wall in the \( z-\theta \) plane.

FIG. 5. (Color) For \( r \) stacks under sufficiently high shear a single heap emerges which moves in the \( \theta \) direction. In this case \( R_1=40\sigma, R_2=65\sigma \), and \( \omega=0.1\tau^{-1} \).
interfacial heap decreases appreciably relative to the convection value. It is easily seen that any acceptable alternative definition of the horizontal axis in this plot will only increase the deviation from the y=x line. Volume-conservation dictates that the same amount of A particles are displaced to r values beyond \( R_{av} \) as there are B particles displaced to r values below \( R_{av} \). Because of the cylindrical geometry, the distance between \( R_{av} \) and the lowest value of r of the interface will be larger than the distance between \( R_{av} \) and the highest value of r of the interface. If anything, a naive consideration of the effect of the moving inner wall would predict a higher average angular velocity. The lower velocity is probably caused by the additional hydrodynamic friction in the narrow region between the extremes of the interface and the inner and outer walls. A detailed analysis of this interfacial heap will be a topic of future research.

C. With shear, starting from randomly mixed systems

Finally, we focus on initially randomly mixed configurations, which are simultaneously phase separating and subjected to shear. In our previous work, we studied phase separation from a randomly mixed configuration in bulk without shear. We showed that the length scale \( R \) characterizing the phase separation initially grows in time according to \( R(t) \propto t^{1/3} \), corresponding to a diffusion limited growth of the domains. After a time \( \tau_{av} = 25\tau \) the scaling law changes to a surface tension driven growth dominated by viscous forces: \( R(t) \propto t^{0.8} - t^{1} \). These simulations concerned the same model as in the current study, only then bulk periodic boundary conditions were used, whereas now we focus on the influence of confinement and curvature combined with shear.

The confinement and curvature will, as before, lead to a preference of a specific stacked structure without shear. At low shear rates this structure may remain, but other stacked structures may become more stable at higher shear rates. For example, in sheared diblock copolymer melts a transition is observed from perpendicular to parallel orientations. At very high shear rates no stable stacked structure may form at all. In particular with reference to the latter case, we expect that there will be a critical shear rate \( \gamma_{av} = 1/\tau_{av} \) separating a regime of stable stacked configurations from a regime of unstable configurations. The reason is the following: Imagine two domains of size R with their centers displaced by a distance of order R in the gradient direction. For shear rates \( \gamma < \gamma_{av} \), the shear rate is so low that viscous, surface tension driven growth has begun before the affine deformation has had any chance to separate and deform the relative position of these two domains. For shear rates \( \gamma > \gamma_{av} \), on the other hand, the shear flow will interfere with the diffusive growth of the domains: the two domains will have been separated and deformed before they have had any chance to diffuse toward each other.

To test the earlier hypotheses, we performed sheared simulations in four different geometries, two simulations with \( R_1 = 25\sigma, R_2 = 65 \), and 70\( \sigma \), respectively, and another two with \( R_1 = 15\sigma, R_2 = 60 \), and 65\( \sigma \), respectively. Note that, ignoring the curvature effect for the moment, the average density, see Eqs. (6) and (8), for the system in Fig. 5. From this we can calculate the angular velocity of the heap in a system containing r-type stacks.

\[
\rho_m(t) = \sum_{i=1}^{N} B_i \cos(m\theta_i(t)),
\]

where \( B_i = \pm 1 \) depending on the particle type and \( \theta_i \) is the polar angle of particle i. We choose an angular mode number \( m=6 \) or 12 to comply with our periodic setup. It is not difficult to show (see Appendix B) that in the continuum limit

\[
\rho_m(t) = X \cos(m\Omega t) + Y \sin(m\Omega t).
\]

The time correlation of \( \rho \) is then calculated as

\[
\langle \rho_m(0)\rho_m(t) \rangle = \frac{1}{2}(X^2 + Y^2)\cos(m\Omega t),
\]

where \( \langle \cdot \cdot \cdot \rangle \) denotes an average over many time origins. An example is shown in Fig. 6. Despite the fact that the interfacial heap is barely visible at lower shear rates, the correlation function Eq. (8) still does a good job at measuring its angular velocity. Figure 7 shows the measured angular velocity of the interfacial heap versus the angular velocity \( d\theta_{HS}/dt \) of a homogeneous solvent (HS) at the average radial position \( R_{av} = \sqrt{(R_1^2 + R_2^2)/2} \). To collect sufficient points for this figure we have performed additional simulations at \( \omega = 0.02 \) and 0.05\( \tau^{-1} \). As expected, for low shear rates the angular velocity of the interface is the same as that of a homogeneous liquid at \( r = R_{av} \). But at higher shear rates the angular velocity of the

FIG. 6. Time-correlation function of the angular difference in A- and B-type density, see Eqs. (6) and (8), for the system in Fig. 5. From this we can calculate the angular velocity of the heap in a system containing r-type stacks.

FIG. 7. Measured angular velocity of the heap vs the angular velocity of a homogeneous fluid at the average position of the interface. The dashed line indicates where both velocities are equal. Circles are measurements from a system with \( R_1 = 40\sigma \) and \( R_2 = 65\sigma \). Squares are measurements from \( R_1 = 40\sigma \) and \( R_2 = 75\sigma \).
shear rate in the slit is approximately equal to $\omega R_1/(R_2 - R_1)$, i.e., about equal to $\omega$ in the systems studied.

All configurations were thoroughly equilibrated and mixed, by means of zero shear rate runs with interactions between unlike particles equal to those between like particles, Eq. (1). After equilibration, shear was imposed by rotating the inner wall with an angular velocity $\omega=0.001, 0.01$, or $0.1 \tau^{-1}$. The resulting flow profiles of these homogeneous systems agreed well with theoretical predictions (not shown). Finally, the repulsion between unlike particles was turned on, Eq. (2), and the mixture started to phase separate.

Free energy calculations suggest that in all these systems $r$ stacks are the most stable configuration without shear. Indeed we found that at low shear rates, $\omega=0.001 \tau^{-1}, r$ stacks are formed and remain stable for the duration of the simulation, see Figs. 8 and 9 (leftmost figures).

When the shear rate was increased to $\omega=0.01 \tau^{-1}$, a transition from steady $r$ stacks to steady $z$ stacks was found for both $R_1=15\sigma$, $R_2=60$ and $R_1=15\sigma$, $R_2=65\sigma$, see Fig. 8 (middle figure). This is analogous to the case of sheared diblock-co-polymer melts attuned to above, where a transition is observed from parallel stacks, with their normals in the gradient direction (here $r$) to perpendicular stacks, with their normals in the vorticity direction (here $z$). 27–29 For $R_1=25\sigma$ and $R_2=65, 70$ multiple (sandwiched) $r$ stacks appear at these high shear rates, see Fig. 9 (middle figure). This may again be a metastable state in which the system is trapped on its way toward a state with just two stacks. It may be very difficult for domains trapped in some metastable state to merge as the only way they can coalesce is by fluctuation of the various interfaces.

In all systems with angular velocities $\omega=0.1 \tau^{-1}$ we observe unsteady complex patterns, see Figs. 8 and 9 (right figures), which do not seem to evolve to any of the stacked states discussed previously. Rather spongolike, streaked structure forms, in which the system appears to be kinetically trapped. While all other simulations are in the regime $\gamma < \gamma_{\text{th}} = 0.04 \tau^{-1}$, those with $\omega=0.1 \tau^{-1}$ all have $\gamma \approx \gamma_{\text{th}}$. When the shear rate is near $\gamma_{\text{th}}$ the diffusive growth is prohibited by convection with the flow. This is substantiated by inspecting the velocity profile, see Fig. 10. At $\omega=0.1$ the velocity profile deviates from that of a homogeneous liquid. High shear rate boundaries emerge at particular values of $r$ (in this case $r=45\sigma$). Diffusion along the gradient direction becomes ineffective across these high shear boundaries. Within each region separated by these boundaries, the effective shear rate is lower and the system is able to form more-or-less stacked states. Indeed, if one is pressed on identifying stacked structures, in Fig. 9 (right figure) there appears to be an inner “$z$ stack” and an outer $z$ stack (mixed with an “$r$ stack”). The high shear boundary allows the outer stack to be shifted relative to the inner one. A horizontal slice would therefore give the appearance of $r$ stacks.

It is interesting to compare these results with those of LB simulations 12–14 published recently. As already mentioned in Sec. I, thermal diffusion is absent from these LB simulations. Moreover, these works focused on the effect of planar shear flow on phase separation in bulk, whereas ours focuses on the effect of confining walls and curvature. In the LB simulations, every effort was undertaken to avoid finite size effects. Finite size effects typically result in quasilinear stripe domains which connect after one or more circuits of the periodic boundary conditions. 12 The stacked domains observed in our work at lower shear rates could be classified as such. In fact, finite size effects are usually so large that it is im-

FIG. 8. (Color) Configurations of the system with $R_1=15\sigma$ and $R_2=60\sigma$ at various angular velocities of the inner wall. The first figure is a top view ($r-\theta$ plane) at $\omega=0.001 \tau^{-1}$, showing the formation of steady $r$ stacks. The second figure is a front view ($r-z$ plane) at $\omega=0.01 \tau^{-1}$ showing the formation of steady $z$ stacks. The third figure is also a front view at $\omega=0.1 \tau^{-1}$, showing one cross section of the complex patterns that emerge and are kinetically trapped.

FIG. 9. (Color) Configurations of the system with $R_1=25\sigma$ and $R_2=70\sigma$ at various angular velocities of the inner wall. The first figure is a top view ($r-\theta$ plane) at $\omega=0.001 \tau^{-1}$, showing the formation of steady $r$ stacks. The second figure is a top view at $\omega=0.01 \tau^{-1}$, showing a probably intermediate state of multiple (sandwiched) $r$ stacks. The third figure is a front view ($r-z$ plane), in perspective and slightly tilted around the $z$ axis, at $\omega=0.1 \tau^{-1}$, showing the complex patterns that emerge.

FIG. 10. Average velocity profile as a function of radial position $r$ in the gap (solid line) for $R_1=25\sigma$, $R_2=70\sigma$, and $\omega=0.1 \tau^{-1}$ (right figure in Fig. 9). The profile for a homogeneous fluid is given by the dashed line. Note the large shear rate at $r=45\sigma$.
possible for MD simulations (of the type we present here) to study phase separation at the scale of the quoted LB simulations.

IV. CONCLUSIONS

We have studied the influence of confinement, curvature, and shear on the phase separation in a 50:50 fluid mixture. When starting from stacked configurations either in the gradient or in the vorticity direction, we observe that these pre-arranged configurations are retained for a very long time, suggesting the presence of large free energy barriers to evolve, if at all, to other configurations. The stacks with their normal in the gradient direction show interesting interfacial perturbations, whose angular velocities decrease relative to the expected angular velocity of a homogeneous fluid at the average interfacial position.

Starting from a randomly mixed configuration, the phase separation evolves toward steady stacks at moderate shear rates. The orientation of these stacks appears, in some cases, to depend on the applied shear rate. At high shear rates we do not observe stacks but complex streaked patterns, which are separated by high shear rate boundaries. The transition from steady stacks to complex patterns takes place at a shear rate equal to the inverse of the crossover time from diffusive to viscous growth of phase-separated domains, as measured in equilibrium simulations. At these shear rates diffusive growth is prohibited by convection with the flow.

For small molecules the time to diffuse over a length scale comparable to the size of the molecule is very short, of the order of several picoseconds. The critical shear rate, allowed to earlier, will in that case be extremely large, probably much larger than can be achieved in experiment. Colloidal particles of size 0.1−1 μm, however, diffuse over their own diameter on time scales of milliseconds to seconds. We therefore believe that our results are relevant to for example microfluidic systems containing such colloidal particles. Certainly bends and corners in microfluidic devices often have the same curvature as those studied here. We may even envisage the construction of a microscopic Taylor–Couette flow cell, with which our results could be validated. We leave this as a challenge to the experimentalists.

ACKNOWLEDGMENTS

A.K.T. thanks FOM and J.T.P. thanks the Netherlands Organisation for Scientific Research (NWO) for financial support.

APPENDIX A: INTERFACIAL FREE ENERGY IN A TAYLOR–COUETTE GEOMETRY

In this appendix we will calculate the interfacial free energy of two fully phase-separated liquids A and B in a Taylor–Couette geometry with inner radius \( R_1 \), outer radius \( R_2 \), height \( Z \), and an overall angle \( \Theta \), (see Fig. 1). The latter angle is relevant for our periodic setup; for a real Taylor–Couette geometry of course \( \Theta = 2 \pi \). We assume a 50:50 (by volume) mixture of the two liquids. We will first treat the case where both liquids are equally wetting the walls, as is the case in our simulations. Experimentally, it is often difficult to attain an equal wettability condition for two different liquids. For completeness, we therefore also treat the case of liquids of different wettability.

1. Free energy calculation for equally wetting liquids

When the surface tension with the wall is equal for both liquids, the configuration of lowest interfacial free energy is simply the configuration of lowest interfacial area \( A_{AB} \) between liquids A and B. Also, the contact angle that the liquid−liquid interface makes with a wall (if it makes contact with a wall at all) is 90 deg. The combination of these two facts leads to the prediction of relatively simple configurations for fully phase separated systems in a Couette cell. Let us explore the possibilities.

First, consider the case of two concentric liquid cylindrical shells. Since the normal of the interface points in the \( r \) direction, we refer to these as \( r \) stacks. The area \( A_{AB} \) between the two liquids simply is

\[
A_{AB} = Z\Theta\sqrt{R_1^2 + R_2^2} / 2. \tag{A1}
\]

Second, we may think of two stacks with their interfaces in the \( r−z \) plane, so-called \( \theta \) stacks. In the case of periodic boundaries in the \( z \) direction there are two liquid interfaces per periodic cell, the total area of which is

\[
A_{AB} = 2(R_2 - R_1)Z. \tag{A2}
\]

Third, two layers may form in the \( r−\theta \) plane, so-called \( \phi \) stacks. Again there are two interfaces, the total area of which is

\[
A_{AB} = \Theta (R_2^2 - R_1^2). \tag{A3}
\]

Finally, consider a semicylindrical drop attached to the outer wall. In this case the total interfacial area is given by

\[
A_{AB} = 2r\Theta \arctan \frac{R_2/d}{\sqrt{1 - R_2^2/d^2}}. \tag{A4}
\]

Here \( d^2 = R_2^2 + r^2 \), where \( r \) is the radius of curvature of the cylindrical drop. It can be found by the condition that the drop must be of volume \( Z\Theta (R_2^2 - R_1^2) / 4 \), i.e., half the volume of the Couette cell and that the interface must touch the wall at right angles.

2. Interfacial free energy calculation for liquids with different wettability

In most practical cases the surface tension \( \gamma_{AW} \) between liquid A and the wall is different from the surface tension \( \gamma_{BW} \) between liquid B and the wall. In that case the lowest interfacial free energy corresponds to a more complex configuration and the contact angle with the wall is no longer 90 deg. The shape of the interface will depend on the relative values of the wall interfacial tensions \( \gamma_{AW} \), \( \gamma_{BW} \), and the interfacial tension \( \gamma_{AB} \) between both liquids. For not too widely different values of the surface tensions, we again get different layered structures whose normals are primarily oriented in the \( r \), \( \theta \), or \( z \) directions.
where \( \gamma_{AW} > \gamma_{BW} \) then liquid A will reside at the inner wall and liquid B at the outer wall. The interfacial free energy is then given by

\[
A = Z\Theta_{L} \left[ R_{1} \gamma_{AW} + R_{2} \gamma_{BW} + \sqrt{\frac{R_{1}^{2} + R_{2}^{2}}{2}} \gamma_{AB} \right].
\]  

(A5)

b. The case of \( r \) stacks

The case of two concentric cylindrical shells is still a possible solution, and the simplest of the three. If we assume \( \gamma_{AW} > \gamma_{BW} \) then liquid A will reside at the inner wall and liquid B at the outer wall. The interfacial free energy is then given by

\[
\frac{d}{dr} \left( \frac{r^{2} \phi}{\sqrt{1 + r^{2} \phi^{2}}} \right) = \lambda r,
\]

(A9)

\[
\frac{R_{1}\dot{\theta}(R_{1})}{\sqrt{1 + R_{1}^{2} \dot{\theta}^{2}(R_{1})}} = \frac{\gamma_{W}}{\gamma_{AB}},
\]

(A10)

\[
\frac{R_{2}\dot{\theta}(R_{2})}{\sqrt{1 + R_{2}^{2} \dot{\theta}^{2}(R_{2})}} = -\frac{\gamma_{W}}{\gamma_{AB}},
\]

(A11)

where \( \lambda = \lambda' / \gamma_{AB} \). Solving for \( \dot{\theta} \) we find

\[
\dot{\theta}^{2} = \frac{\left( C + \frac{1}{2} \lambda r^{2} \right)^{2}}{r^{4} - r^{2} \left( C + \frac{1}{2} \lambda r^{2} \right)},
\]

(A12)

where \( C \) is a constant. From Eq. (A10) we obtain

\[
R_{1}\dot{\theta}(R_{1}) = \frac{\gamma_{W} \gamma_{AB}}{\sqrt{1 - (\gamma_{W} / \gamma_{AB})^{2}}},
\]

(A13)

which must be consistent with Eq. (A12). Differentiating the latter, multiplying by \( R_{1} \), and comparing the result with Eq. (A13), we find after some rearrangements

\[
\frac{C}{R_{1}} + \frac{1}{2} \lambda R_{1} = -\frac{\gamma_{W}}{\gamma_{AB}},
\]

(A14)

Similarly, from Eqs. (A11) and (A12), we obtain

\[
\frac{C}{R_{2}} + \frac{1}{2} \lambda R_{2} = \frac{\gamma_{W}}{\gamma_{AB}},
\]

(A15)

Solving for \( C \) and \( \lambda \) we get

\[
C = \frac{R_{1} R_{2}}{R_{2} - R_{1}} \frac{\gamma_{W}}{\gamma_{AB}},
\]

(A16)

\[
\lambda = 2 \left( \frac{\gamma_{W}}{\gamma_{AB}} \right) \frac{1}{R_{1}/R_{2} - 1}.
\]

(A17)

The shape of the interface is now known, and only its starting point \( \theta(R_{1}) \) at the wall remains to be determined. This is not difficult, as half the total volume must be occupied by fluid A. A little more algebra yields

\[
\theta(R_{1}) = \frac{\Theta_{L}}{4} - \int_{R_{1}}^{R_{2}} \frac{R_{2}^{2} - R_{1}^{2}}{R_{2}^{2} - R_{1}^{2}} \frac{r^{2} \phi}{\sqrt{1 + r^{2} \phi^{2}}} \left( C + \frac{1}{2} \lambda r^{2} \right).
\]

(A18)

The interfacial free energy, finally, is given by

\[
A = Z(\gamma_{AW} L_{AW} + \gamma_{BW} L_{BW} + \gamma_{AB} L_{AB})
\]

(A19)

with

\[
L_{AW} = 2 R_{1} \theta(R_{1}) + 2 R_{2} \theta(R_{2}),
\]

(A20)

\[
L_{BW} = R_{1} (\Theta_{L} - 2 \theta(R_{1})) + R_{2} (\Theta_{L} - 2 \theta(R_{2})),
\]

(A21)
\[ L_{\text{AB}} = 2 \int_{R_1}^{R_2} dr \sqrt{\frac{1}{1 - \left( \frac{z}{r} + \frac{1}{2} \lambda r^2 \right)^2}}. \] \tag{A22}

It is perhaps illuminating to define
\[ R_1 \theta(R_1) = \tan(\pi/2 - \alpha), \] \tag{A23}
where \( \alpha \) is the angle between the AB interface and the inner cylinder. Equation (A13) may then be rewritten as Young’s equation
\[ \gamma_{\text{AW}} - \gamma_{\text{BW}} + \gamma_{\text{AB}} \cos \alpha = 0. \] \tag{A24}

**c. The case of \( z \) stacks**

For the \( z \) stacks the profile can be derived in a similar fashion, in which case we choose our coordinates such that fluid A is centered around the plane \( z = 0 \). The upper interface with fluid B is then described by a function \( z(r) \), again in cylindrical coordinates. For reasons of symmetry we assume that the interface is independent of \( \theta \) and that another AB interface (within our periodic cell) is situated at \( Z - z(r) \).

Now the Lagrangian to be minimized is
\[ L = \int_{R_1}^{R_2} dr [\gamma_{\text{AB}} \sqrt{1 + \dot{z}^2} - \lambda' \dot{z}] + \gamma_{\text{W}} z(R_1) R_1 + z(R_2) R_2, \] \tag{A25}
where \( \dot{z} = dz/dr \) and again \( \lambda' \) is a Lagrange multiplier to constrain the volume (now the area in the \( r-z \) plane). The resulting profile is given by
\[ z(r) = z(R_1) + \int_{R_1}^{r} dr \frac{C + \frac{1}{2} \lambda r^2}{\sqrt{\lambda^2 - \left( C + \frac{1}{2} \lambda r^2 \right)^2}}, \] \tag{A27}
where \( C \) and \( \lambda \) are the same as in Eqs. (A16) and (A17). The value of \( z(R_1) \) can again be fixed by setting the volume occupied by fluid A equal to half the total volume. This yields
\[ z(R_1) = \frac{Z}{4} - \int_{R_1}^{R_2} dr \frac{R_2^2 - r^2}{R_1^2 - r^2} \frac{C + \frac{1}{2} \lambda r^2}{\sqrt{\lambda^2 - \left( C + \frac{1}{2} \lambda r^2 \right)^2}}. \] \tag{A27}

The interfacial free energy is then given by
\[ A = \Theta(A_{\text{AW}} A_{\text{BW}} + \gamma_{\text{BW}} A_{\text{BW}} + \gamma_{\text{AB}} A_{\text{AB}}), \] \tag{A28}
\[ A_{\text{AW}} = 2 R_1 z(R_1) + 2 R_2 z(R_2), \] \tag{A29}
\[ A_{\text{BW}} = R_1 (Z - 2 \dot{z}(R_1)) + R_2 (Z - 2 \dot{z}(R_2)), \] \tag{A30}
\[ A_{\text{AB}} = 2 \int_{R_1}^{R_2} dr \sqrt{1 \left( \frac{z}{r} + \frac{1}{2} \lambda r^2 \right)^2}. \] \tag{A31}

**APPENDIX B: DERIVATION OF Eqs. (7) and (8)**

The continuum approximation of Eq. (7) reads
\[ \rho_m(t) = \rho \int_0^{\pi/3} d\theta \cos(m\theta) \int_{R_1}^{R_2} dr \left( 1 - 2H(r - R(\theta, t)) \right) \] \tag{B1}
where \( H(x) \) is Heaviside’s function, i.e., \( H(x) = 0 \) for \( x < 0 \) and \( H(x) = 1 \) for \( x \geq 0 \), and where \( m \) is a multiple of 6. Using the soliton-like character expressed in Eq. (5), we transform this into
\[ \rho_m(t) = \rho Z \int_0^{\pi/3} d\theta \cos(m\theta) R^2(\theta - \Omega t, 0) \] \tag{B2}
\[ = \rho Z \int_{-\Omega t}^{\pi/3 - \Omega t} d\theta \cos(m\theta + m\Omega t) R^2(\theta, 0) \] \tag{B2}
\[ = \rho Z \cos(m\Omega t) \int_0^{\pi/3} d\theta \cos(m\theta) R^2(\theta, 0) \] \tag{B2}
\[ - \rho Z \sin(m\Omega t) \int_0^{\pi/3} d\theta \sin(m\theta) R^2(\theta, 0) \] \tag{B2}
\[ = X \cos(m\Omega t) + Y \sin(m\Omega t). \] \tag{B2}

Using this result, we calculate the time correlation function
\[ \langle \rho_m(t) \rho_m(0) \rangle = \frac{1}{T} \int_0^T d\tau \rho_m(t + \tau) \rho_m(\tau) = \frac{1}{T} \int d\tau \rho_m(t + \tau) \rho_m(\tau) \] \tag{B3}
\[ + Y^2 \cos(m\Omega t), \] \tag{B3}
where \( T \) is a multiple of \( 2\pi/(m\Omega) \).

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